Liquid Chromatography using ion-trap mass spectrometry with wideband activation for the determination of microcystins in water

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Introduction

Microcystins are a chemically diverse group of heptapeptide toxins that are produced by cyanobacteria (blue-green algae) and over 65 have been characterised, to-date. Microcystins are specific inhibitors of protein phosphatases, are potent tumour promoters, and strict requlatory control is required to comply with the World Health Organisation guideline limit of 1 µg/L. Electrospray ion-trap mass spectrometry (MS) was applied to the determination of microcystins in cyanobacteria and water samples.

Hypothesis

Electrospray ion-trap mass spectrometry (MS) can detect and differentiate various congeners and analogues of microcystins in cyanobacteria and water samples.

Methods

Sample preparation involved C-18 solid phase extraction but large variations in extraction efficiencies were observed for individual microcystins, MC-LR, MC-YR, MC-RR and MC-LA. Both C-18 and amide columns were used for the separation of microcystins using liquid chromatography (LC) and both collision induced dissociation (CID) and MS/MS studies can been carried out simultaneously, using electrospray interfacing.

Results

Microcystins have a unique C-20 β-amino acid side chain (adda) and the cleavage of part of this moiety gives rise to a characteristic fragment ion at *m/z* 135 that allows the MS detection of unknown microcystins using source CID. MS studies revealed that the loss of a water molecule is typical of microcystins but to obtain abundant characteristic fragment ions from microcystins, WideBand activation together with a high collision energy was used. In this mode, both the parent ion, $[M+H]^+$ and the $[M+H-H_2O]^+$ ions were trapped and fragmentation of the latter produced spectral data that were characteristic of individual microcystins.

Conclusion

Liquid chromatography using ion-trap mass spectrometry with wideband activation can characterize individual microcystins in water.